Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

CO release from Mn(I)-based photoCORMs with Single Photons in the Phototherapeutic Region

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1. Experimental Section

Materials and Instruments

All reagents and solvents were of commercial grade and used without further purification. L1 and was synthesized similarly to reported procedures.[1–4] The IR spectra were recorded using a Perkin-Elmer Spectrum-One FT-IR and ^{1}H-NMR spectra obtained at 298 K on Varian Unity Inova 500 MHz instrument. A Varian Cary 50 UV-Vis spectrophotometer was employed for UV-Vis spectra at room temperature.

Synthesis

$[MnBr(CO)_3(L1)]$ (**1**)

0.174 g (0.63 mmol) of Bromopentacarbonylmanganese(I) was dissolved in dichloromethane (4mL) and a solution of 0.197 g (0.63 mmol, 1 eq) of L1 in dichloromethane (30 mL) was added in the dark at room temperature. The flask was covered in foil to protect from light and allowed to stir in the dark for 3 days after which a dark green precipitate appeared. The solvent was reduced to 15 mL, precipitate filtered and washed with 2mL of cold dichloromethane and complex isolated as a dark green solid (0.280 g, 84% yield). $C_{20}H_{14}BrClMnN_3O_4$ Anal. Calcd: C, 45.27; H, 2.66; N, 7.92. Found: C, 45.36; H, 2.53; N, 7.84. IR (KBr, cm^{-1}): 2016 (s), 1932 (s), 1912 (s), 1614 (w), 1590 (m), 1410 (m), 1377 (s), 1314 (s), 1172 (m), 1073 (m), 1036 (m), 867 (w). ^{1}H-NMR ($CDCl_3$): 9.32 (d, 1H), 8.95 (d, 1H), 7.78 (m, 1H), 7.70 (s, 1H), 7.32 (d, 2H), 6.92 (d, 2H), 3.25 (s, 6H).

$[MnBr(CO)_3(L2)]$ (**2**)

A similar procedure to **1** was employed using 0.0726 g (0.26 mmol) of Bromopentacarbonylmanganese(I) and 0.1008 g (0.26, 1eq) of L2 in dichloromethane. After 3

days of stirring in the dark the solvent was reduced to 10mL and 50mL of hexanes was added. The precipitate was filtered and washed with cold hexanes and complex isolated as a dark green solid (0.115 g, 76% yield). Anal. Calcd: C, 51.93; H, 3.02; N, 9.32. Found: C, 51.84; H, 3.07; N, 9.25. IR (KBr, cm^{-1}): 2022 (s), 1937(s), 1920 (s), 1604 (m), 1591 (m), 1448 (m), 1364 (s), 1177 (w), 749 (w) ^{1}H-NMR ($CDCl_3$): 9.36 (d, 1H), 9.00 (d, 1H), 8.50 (d, 1H), 7.71 (m, 1H), 7.44 (t, 1H), 7.35 (t, 1H), 7.24 (m, 1H, overlaps with $CDCl_3$), 7.12 (d, 2H), 7.02 (s, 1H), 6.79 (d, 2H), 3.08 (s, 6H).

2. ^{1}H NMR Spectra

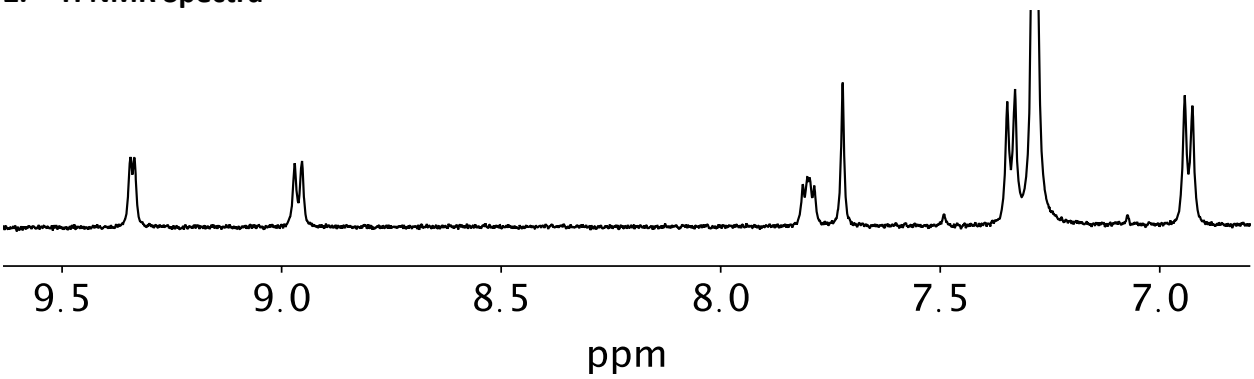

Fig. S1. ^{1}H NMR spectrum of **1** in $CDCl_3$ at 298K (not shown; 3.25 ppm, s, 6H).

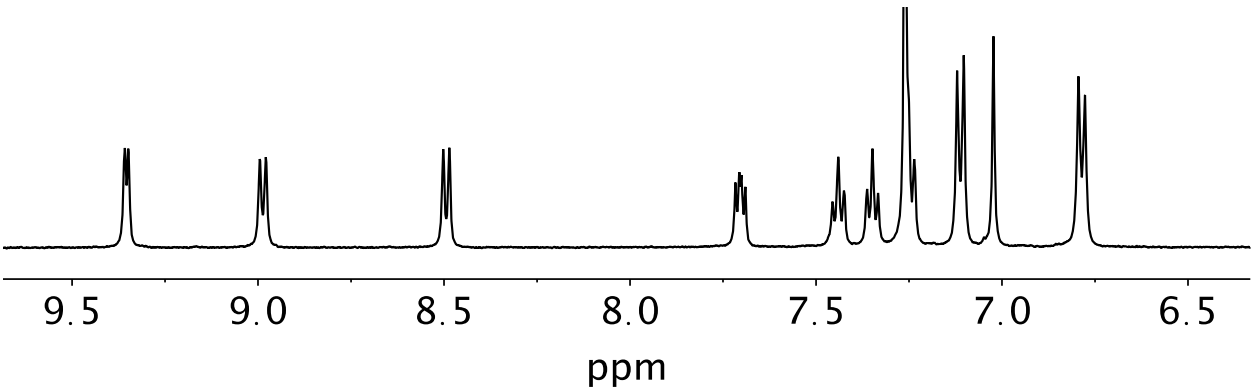

Fig. S2. ^{1}H NMR spectrum of **2** in $CDCL_3$ at 298K (not shown; 3.08 ppm, s, 6H).

3. Crystallography

Data were collected on a Bruker D8 Quest single crystal X-ray diffractometer (PHOTON 100 CMOS detector) with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by the ω-scan technique in the range $5.4 \leq 2\theta \leq 50$ for (for both **1** and **2**). All data were corrected for Lorentz and polarization effects.[5] All the structures were solved with the aid of *SHELXT* program using intrinsic phasing.[6] The structures were then refined by a full-matrix least squares procedure on $\mathbf{F}^2$ by *SHELXL*.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Multi-scan absorption corrections are applied using SADABS[2]. Calculations were performed using the *OLEX*2[8] and *SHELXTL*™ (V 6.14)[9] program packages. The experimental details are listed in Table S1 and CCDC 2026578 and 2026579 for **1** and **2** respectively.

Table S1. Crystal data and structure refinement parameters for **1** and **2**

	1	**2**
Empirical formula	$C_{20}H_{14}MnN_3O_4BrCl$	$C_{26}H_{18}MnN_4O_3SBr$
FW	530.64	601.36
Temp(K)	298	150
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pcab*	$P2_1/c$
a (Å)	7.6931 (7)	13.6697 (17)
b (Å)	17.5230 (15)	22.226 (3)
c (Å)	30.345 (3)	8.017 (1)
a (°)	90	90
b (°)	90	99.760 (3)
g (°)	90	90
Z	8	4
V (Å^3)	4090.7 (6)	2400.5 (5)
Density (calcd) (Mg m^{-3})	1.723	1.724
Abs coeff (mm^{-1})	2.76	2.78
No. of unique reflns.	3640	4252
R_1[b]	0.080	0.100
wR_{2c}	0.163	0.193
GOF[a] on F^2	1.12	1.04

[a] GOF = $[\Sigma[w(Fo^2 - Fc^2)^2]/(No - Nv)]^{1/2}$ (No = number of observations, Nv = number of variables).
[b] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$.
[c] $wR2 = [(\Sigma w(Fo^2 - Fc^2)^2/\Sigma|Fo|^2)]^{1/2}$.

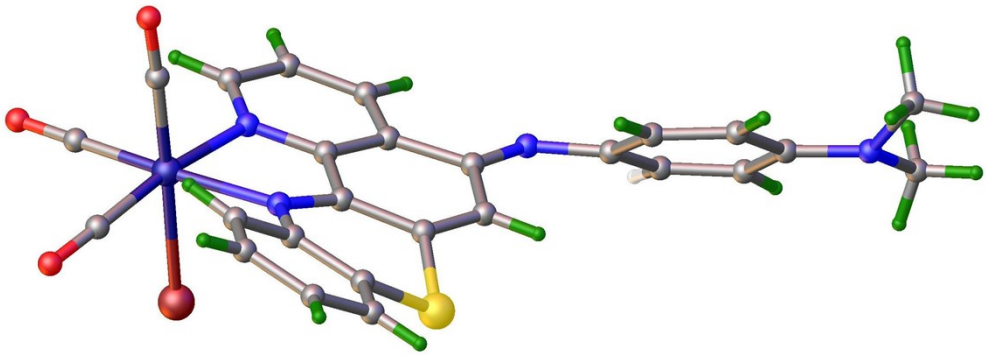

Fig. S3. ORTEP drawing of **2** with ellipsoids at 50% probability level**.**

4. Supplementary Figures

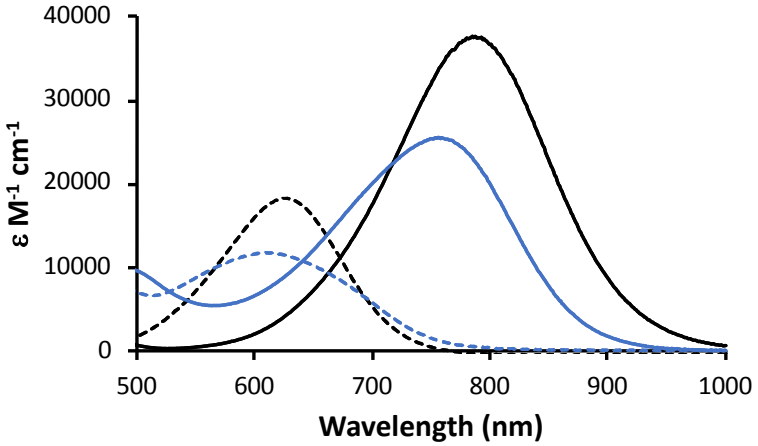

Fig. S4. The electronic spectrum of **1** (black trace), L1 (black dashed trace), **2** (blue trace) and L2 (blue dashed trace) in $CHCl_3$.

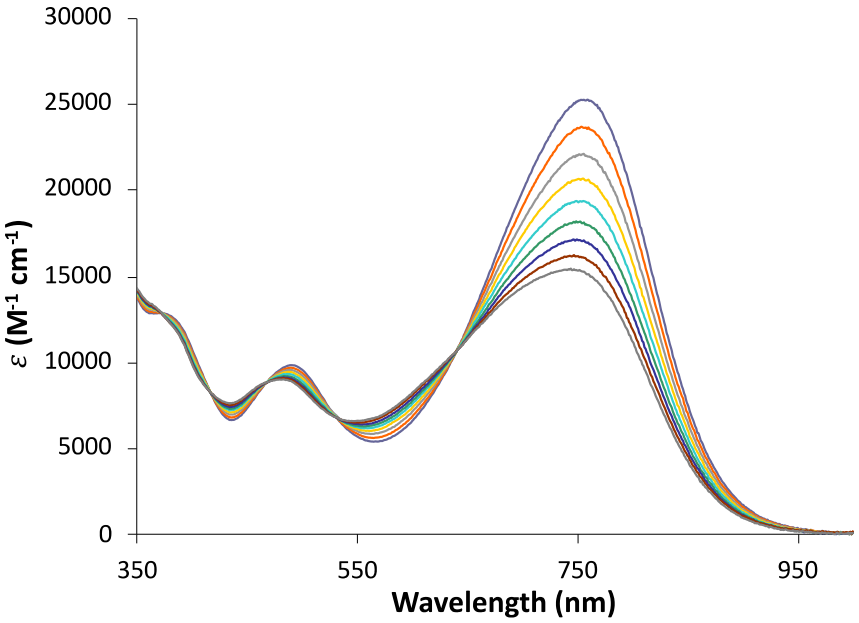

Fig. S5. Spectral Changes of **2** upon exposure to 730 nm light in 2 min intervals in aerobic $CHCl_3$. The light was placed 1 cm away from the cuvette for each exposure.

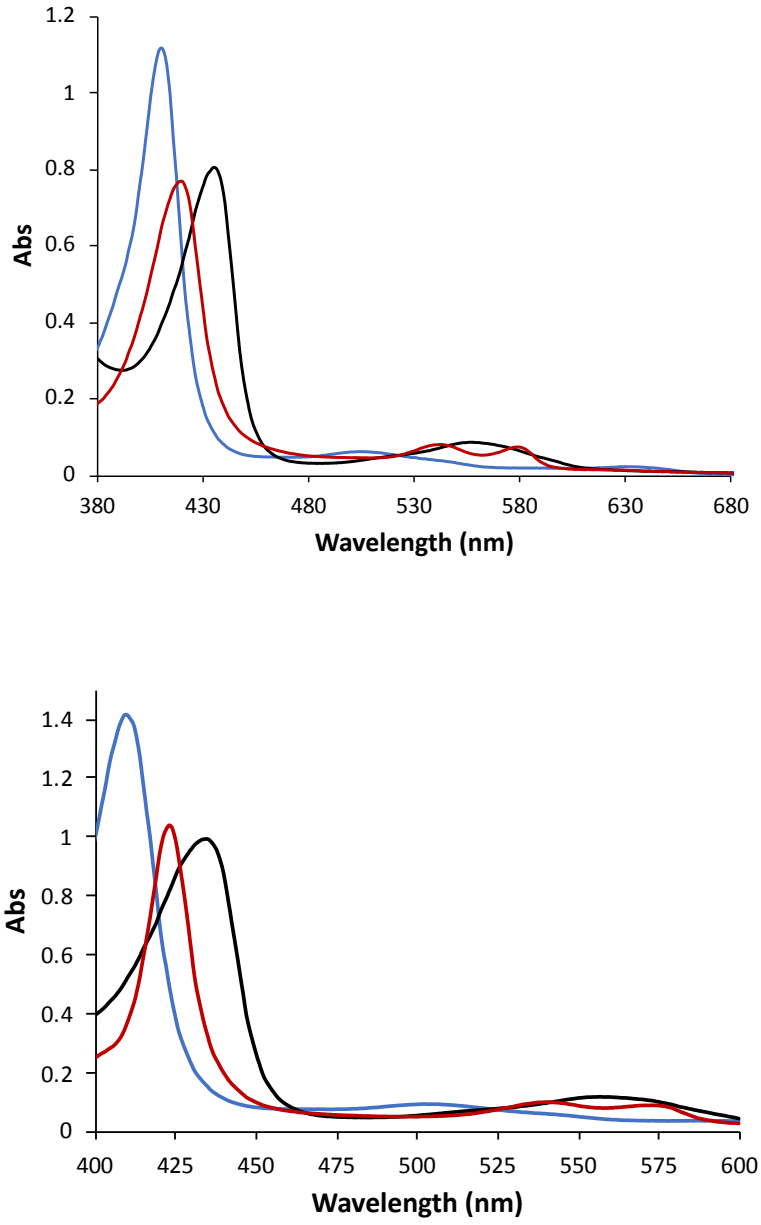

Fig. S6. UV-vis traces from the Myoglobin assay with a $CHCl_3$ solution of **1** (top) and **2** (bottom) at 298K: blue trace, oxidized Mb; black trace, reduced Mb; red trace, COMb.

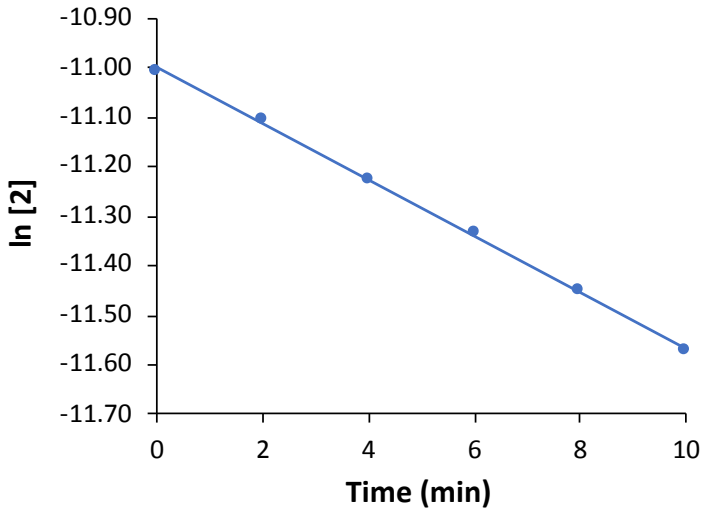

Fig. S7. The ln[**2**] vs time plot used to the find the k_{CO} of **2** (0.0566 ± 0.0008 min^{-1}) in aerobic $CHCl_3$ after exposure to 730 nm light.

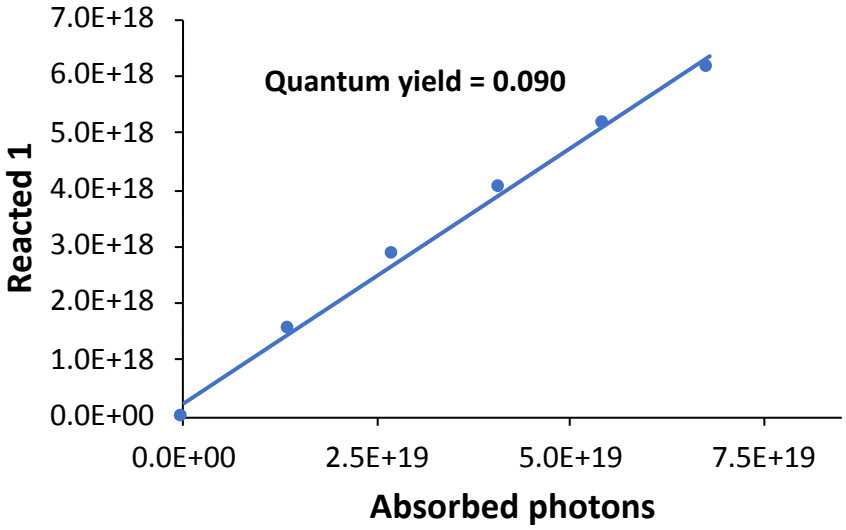

Fig. S8. The quantum yield (Φ) measurement of photolysis at 730 mn (30.80 mW) of **1** (25 μM) (Φ = 0.090 ± 0.004) in aerobic $CHCl_3$. Calculated from the slope of the $N_{reacted}$ vs N_{abs} plot.

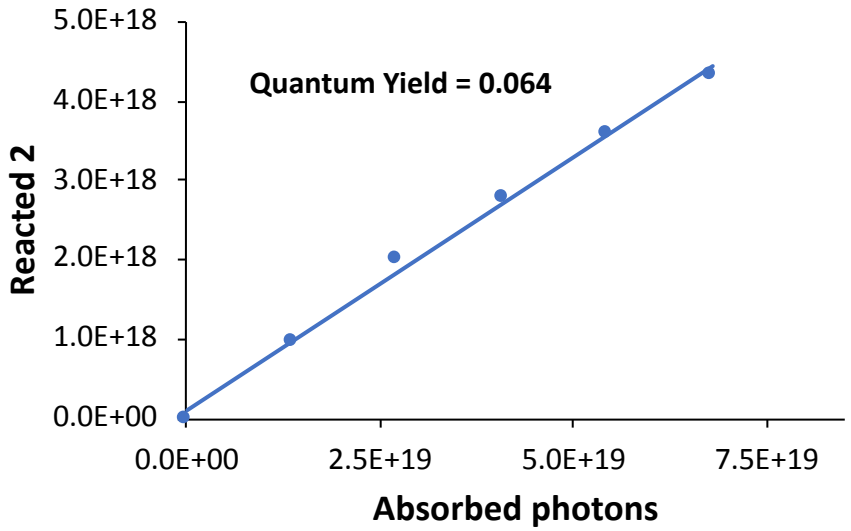

Fig. S9. The quantum yield (Φ) measurement of photolysis at 730 mn (30.80 mW) of **2** (25 μM) (Φ = 0.064 ± 0.002) in aerobic $CHCl_3$. Calculated from the slope of the $N_{reacted}$ vs N_{abs} plot.

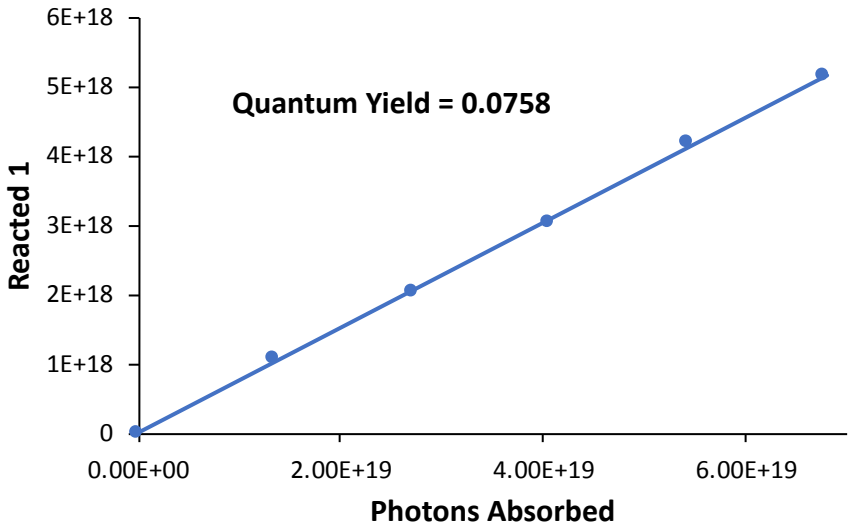

Fig. S10. The quantum yield (Φ) measurement of photolysis at 730 mn (30.80 mW) of **1** (35 μM) (Φ = 0.0758 ± 0.0009) in anaerobic $CHCl_3$. Calculated from the slope of the $N_{reacted}$ vs N_{abs} plot.

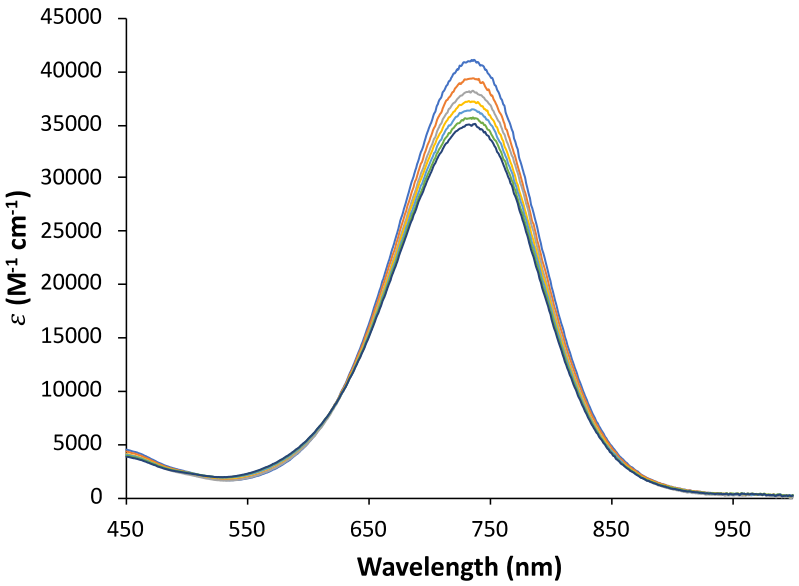

Fig. S11. Spectral Changes of **1** upon exposure to 730 nm light in 4 min intervals in PBS with 1%DMSO.

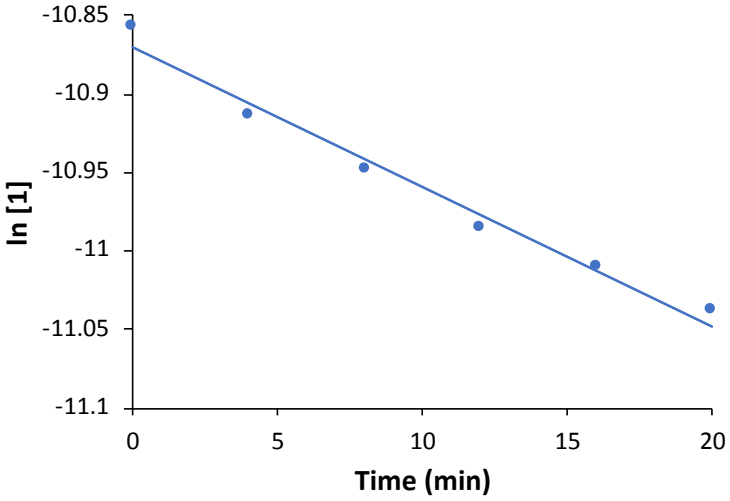

Fig. S12. The ln vs time plot used to the find the k_{CO} of **1** (0.0088 ± 0.0006 min^{-1}) in aerobic 1%DMSO/PBS after exposure to 730 nm light.

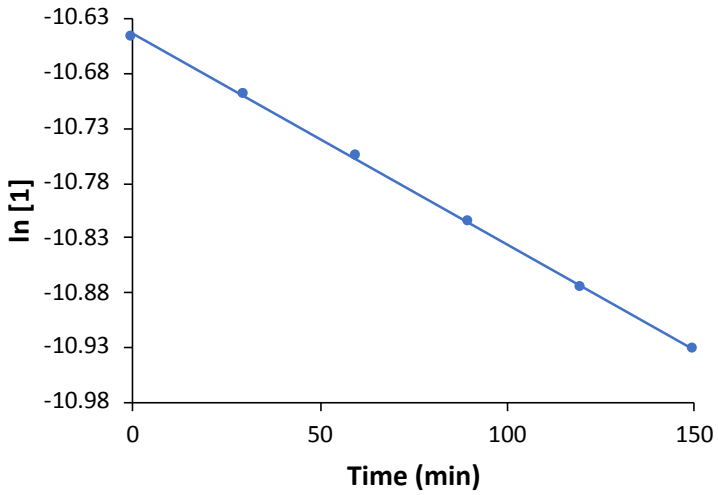

Fig. S13. The ln vs time plot used to the find the k_{CO} of **1** under dark conditions (0.00190 ± 0.00002 min^{-1}) in aerobic 1%DMSO/PBS.

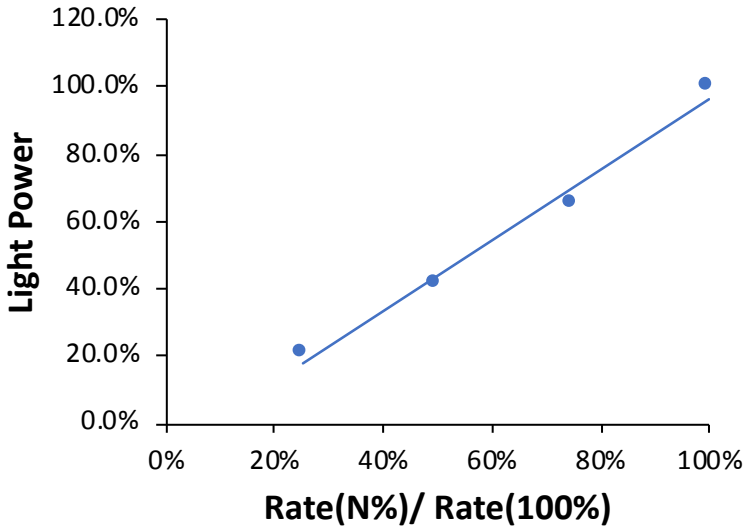

Fig S14. Comparison of k_{CO} release rates compared to power of light source output. Proportionality constant = 1.04 ± 0.09.

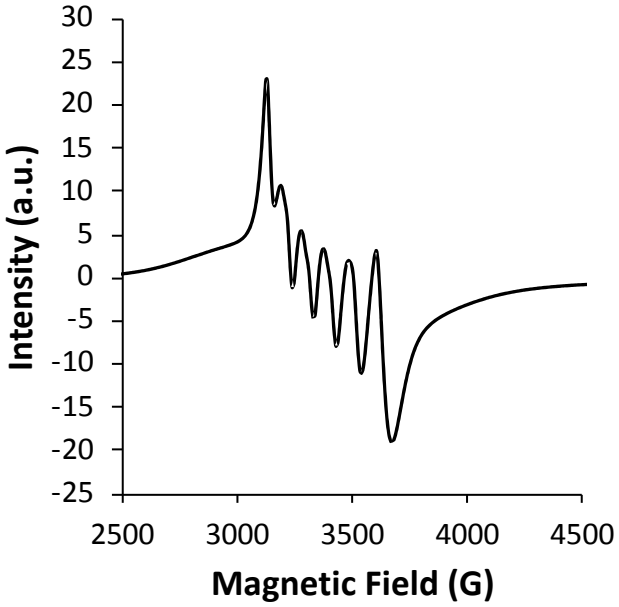

Fig. S15. X-band EPR spectrum of photolyzed **1** in MeCN.

5. Density Functional Studies

Computational Methods

Density functional theory (DFT), as implemented in the ADF program (version 2019.103),[10] was used for the ground state structure optimizations without any constrains. The revPBE functional,[11] including the Grimme D3 corrections and the Becke-Johnson damping,[12] was used. The TZP[13,14] basis sets were used for all atoms, and the relativistic Scalar ZORA[15] approach was applied for the Mn. The COSMO[16–18] approach was used as the implicit solvent model, where dichloromethane was used as the solvent. For all calculations, the numerical quality was set to "normal". Vibrational frequency calculations were performed at 298.15K and 1 atm to confirm the local minima *(i.e.* no imaginary frequency). Time dependent DFT (TDDFT) method was used for calculating the vertical excited states using the ground state optimized structures. The range separated LYC-PBE[19] functional with the Gamma value of 0.22 was employed. The TZ2P basis sets were used for all atoms, the Scalar ZORA approach was used for Mn, and the COSMO implicit solvent model was employed.

DFT Results

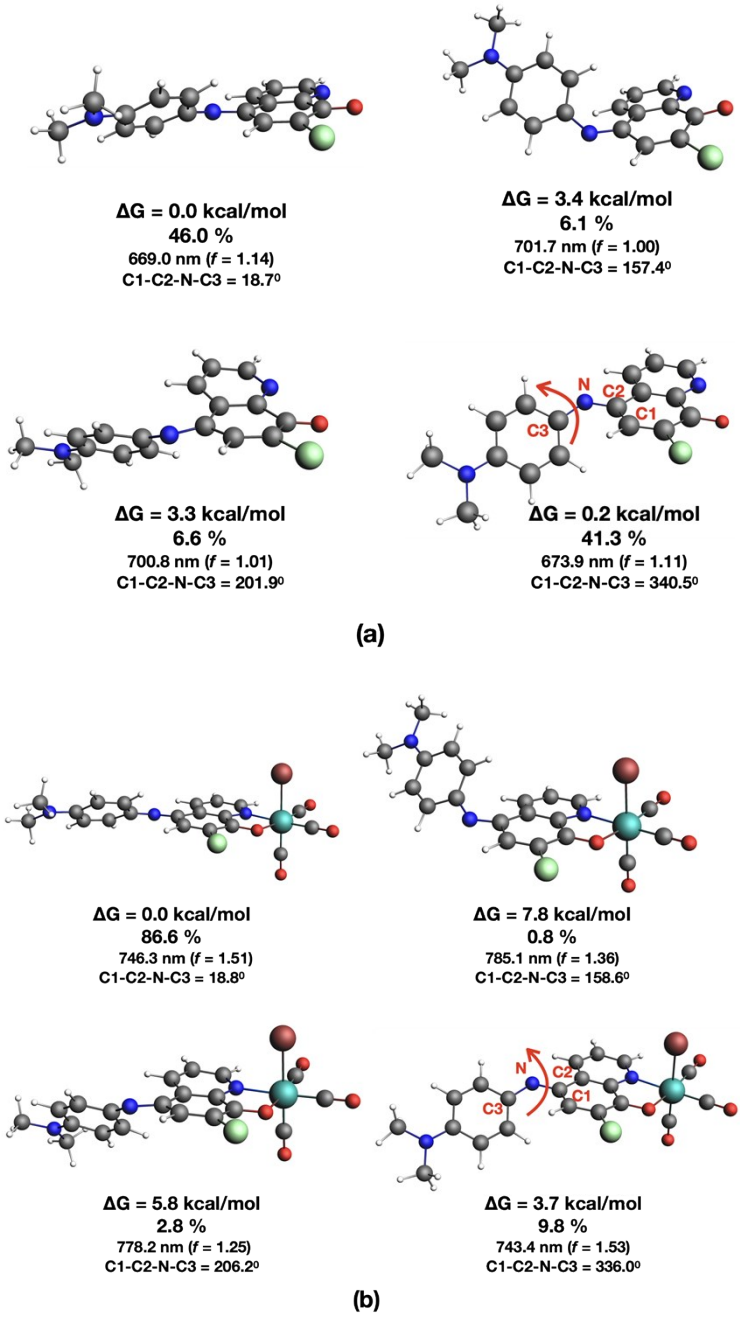

Fig. S16. Relative Gibbs free energy (in kcal/mol), fraction of molecules in the ground state ensemble for the conformation (%), excitation wavelength (oscillator strength), C1-C2-N-C3 torsion angle (in ^{0}) of the conformers of (a) L1 and (b) **1**.

In the case of L1, two energetically equivalent conformers, consisting the C1-C2-N-C3 torsion angle 18.7^0 and 340.5^0, were found. The former and latter conformers represent 46% and 41%vof the molecules in the ground state ensemble, respectively. In the case of **1**, the most stable conformer has the C1-C2-N-C3 torsion angle of 18.8^0, representing 87% of complexes in the ground state ensemble.

TD-DFT Results

L1:

C1-C2-N-C3 = 18.7^0

orbitals			weight
81a	->	82a	0.9402

C1-C2-N-C3 = 157.4^0

orbitals			weight
81a	->	82a	0.9325

C1-C2-N-C3 = 201.9^0

orbitals			weight
81a	->	82a	0.9318

C1-C2-N-C3 = 340.5^0

orbitals			weight
81a	->	82a	0.9401

1:

C1-C2-N-C3 = 18.8^0

orbitals			weight
132a	->	133a	0.9298

C1-C2-N-C3 = 158.6^0

orbitals		weight
132a	-> 133a	0.9272

C1-C2-N-C3 = 206.2^0

orbitals		weight
132a	-> 133a	0.9311

C1-C2-N-C3 = 336.0^0

orbitals		weight
132a	-> 133a	0.9331

Cartesian coordinates of the calculated structures and their energies

L1:

C1-C2-N-C3 = 18.7^0

H	8.083296861261	14.446240935213	25.742356511266
H	8.125752623569	14.592190677906	27.519516088590
Cl	2.492996440329	8.842100910330	23.062892787366
H	7.087294365267	16.273462054479	28.196660705057
H	5.313222593480	16.136140319501	28.254716396339
C	6.181662945952	16.234333730197	27.585711728493
O	0.827828844338	9.228653364736	20.614937656284
N	-0.352529176174	11.568190516065	19.718642211621
N	2.057468184711	13.990153162341	23.144661036181
N	6.275751470779	15.086729414123	26.675687398093
H	7.277863316969	13.219581897439	26.767905174237
C	7.507800917764	14.290233946668	26.669484072059
H	6.092903861563	17.178257041781	27.025561801987
C	-0.910484527378	12.718767775121	19.320842007519
H	-1.590841371613	12.656343913540	18.465812458629
C	-0.663052139999	13.963030622856	19.936270022003
H	-1.152272671859	14.865221770132	19.565105421845
C	0.213742853605	14.010827484500	21.010677272402
H	0.453756350298	14.946665578978	21.515739203887
C	0.810837037315	12.815696206684	21.467056352042
C	1.767627226780	12.817186883782	22.585725992726
C	2.256310516274	11.537661666326	23.039374999881
H	2.849245907089	11.500383358731	23.952009908072
C	1.924930388168	10.370322743019	22.408109596325

C	1.077666406623	10.300361071701	21.205059250944
C	0.492682511898	11.613146186362	20.781626181121
C	3.127051086004	14.195464450305	23.980152917393
C	4.364825116896	13.479773470918	23.945708409128
H	4.528208224675	12.729317831781	23.172246827427
C	5.401861494553	13.784284051544	24.808377329353
H	6.343180179025	13.247089381511	24.706407638501
C	5.268465254735	14.816141596456	25.791537907852
C	4.056250996251	15.578290007156	25.786562870186
H	3.924736007284	16.400801079625	26.487380822464
C	3.041756751165	15.290169844259	24.892987087720
H	2.124836250240	15.882312485178	24.899310032518

C1-C2-N-C3 = 157.4^0

H	0.765784514653	18.989047181961	19.390071838279
H	1.276344344484	20.631228621964	19.847691129001
Cl	3.263306225721	9.121439013253	22.764400277706
H	1.178558888878	21.269011019040	21.831584819484
H	2.141626158805	20.375635207559	23.037150047801
C	1.264260429937	20.323417842379	22.373644302614
O	1.602965382882	9.291344655067	20.281763910256
N	-0.290565681688	11.210946189367	19.678094259009
N	1.913588189704	13.940565133302	23.185866033124
N	1.400961337841	19.233130117136	21.400974386831
H	2.505274026250	19.365620647604	19.583023902372
C	1.495347237441	19.567623217121	19.974936654281
H	0.361974535168	20.190200172598	22.989674311219
C	-1.214154718310	12.147634880686	19.429631504022
H	-1.911754519584	11.936840154181	18.613286008760
C	-1.337003742667	13.335637151832	20.176902453489
H	-2.149963691202	14.033803266199	19.972245348334
C	-0.408726112167	13.591620215992	21.176147439033
H	-0.482606989028	14.498657592662	21.773176382405
C	0.626952140002	12.661650183434	21.422409079828
C	1.606254849020	12.830092652329	22.517233100953
C	2.294870371691	11.643843663499	22.964149972051
H	2.916565398837	11.740181226714	23.855384479580
C	2.288464585884	10.483099808836	22.240105940966
C	1.526656475118	10.313863200922	20.994295995364
C	0.599613471237	11.449714874052	20.676658583733
C	1.750378029196	15.212863871331	22.689807246787
C	1.852914405224	15.564239586893	21.309236691931
H	2.057294163184	14.784781215174	20.575528320670
C	1.764773846115	16.876571422965	20.888855467926

H	1.904635335113	17.099072825181	19.832627188822
C	1.529319469612	17.938529006974	21.821450251192
C	1.467356291209	17.595388962414	23.209593224703
H	1.321561847212	18.371005579939	23.959060398606
C	1.610795049842	16.282666024926	23.622131279747
H	1.575883857539	16.039890133863	24.686112045026

C1-C2-N-C3 = 201.9^0

H	-4.375782568742	16.750400651389	24.272832982143
H	-4.480913023270	18.485209711308	23.878092370467
Cl	2.992704373663	9.034760893054	23.002854384702
H	-3.035720042197	19.705412220510	24.743400291308
H	-1.353538715968	19.555660970264	24.178466634674
C	-2.158732844641	19.052933386271	24.735581495107
O	1.248079786952	9.125578783998	20.573497939094
N	0.262342348778	11.378998870203	19.319892453452
N	1.332322230496	13.742789546667	23.551761874322
N	-2.521670053396	17.781869704745	24.097970130118
H	-3.982904638397	17.324000216255	22.622961158399
C	-3.916547882840	17.567150362418	23.693912354264
H	-1.827035704365	18.895734421994	25.773872370870
C	-0.172927339413	12.494506951348	18.721740981393
H	-0.581947205777	12.375918659978	17.713722436677
C	-0.094280287563	13.772261181757	19.309698856291
H	-0.403109438499	14.656249261215	18.749862193245
C	0.385228584847	13.878820198421	20.607787576394
H	0.460044449337	14.854162082640	21.085360009634
C	0.787147565987	12.715008519072	21.302169350916
C	1.377766324033	12.757011675754	22.657386935753
C	2.155462046314	11.611365229188	23.063968626054
H	2.699869654573	11.694972091749	24.005531316682
C	2.122179997913	10.426722130477	22.380898560590
C	1.356238608404	10.232232942976	21.141816679872
C	0.762186502374	11.489547663340	20.578238165639
C	0.358794686386	14.712358075628	23.606455689476
C	-1.000027192885	14.530164908123	23.205431804134
H	-1.310571105826	13.569148511072	22.795843423568
C	-1.945605380217	15.521252945991	23.384024919133
H	-2.978777247141	15.316117356841	23.109210491817
C	-1.592199554824	16.790513402005	23.947363874095
C	-0.238442529273	16.966406046758	24.377287888600
H	0.072948522131	17.903180946538	24.835765781453
C	0.685859948431	15.946149536725	24.242744092813
H	1.709273289724	16.090033591320	24.594464311687

C1-C2-N-C3 = 340.5^0

H	3.847400000000	12.223100000000	29.358900000000
H	3.876400000000	13.395600000000	30.698900000000
Cl	3.101500000000	8.985000000000	22.635100000000
H	4.393800000000	15.385600000000	30.342100000000
H	3.399900000000	16.335800000000	29.209100000000
C	4.112100000000	15.500600000000	29.292300000000
O	1.193500000000	9.366600000000	20.384600000000
N	-0.111400000000	11.682100000000	19.625400000000
N	1.695300000000	13.865100000000	23.540400000000
N	3.511900000000	14.248600000000	28.824300000000
H	2.318300000000	12.916600000000	29.977500000000
C	3.377300000000	13.131700000000	29.762900000000
H	5.014400000000	15.746500000000	28.711700000000
C	-0.708700000000	12.827200000000	19.276400000000
H	-1.312500000000	12.799600000000	18.363900000000
C	-0.594900000000	14.023700000000	20.013400000000
H	-1.103700000000	14.926700000000	19.672500000000
C	0.165600000000	14.019400000000	21.174500000000
H	0.275500000000	14.910300000000	21.792500000000
C	0.817200000000	12.830300000000	21.567700000000
C	1.604400000000	12.759700000000	22.807200000000
C	2.291600000000	11.525200000000	23.093400000000
H	2.982200000000	11.495600000000	23.934600000000
C	2.170100000000	10.428300000000	22.286300000000
C	1.316500000000	10.388100000000	21.088500000000
C	0.646900000000	11.682800000000	20.750700000000
C	2.126800000000	13.882800000000	24.840300000000
C	1.956900000000	12.825700000000	25.787500000000
H	1.407000000000	11.930300000000	25.496600000000
C	2.386900000000	12.951900000000	27.095300000000
H	2.184100000000	12.142900000000	27.794600000000
C	3.051700000000	14.137100000000	27.543900000000
C	3.178600000000	15.216900000000	26.612400000000
H	3.647000000000	16.150400000000	26.917800000000
C	2.700400000000	15.097400000000	25.322100000000
H	2.795400000000	15.930600000000	24.623300000000

2:

C1-C2-N-C3 = 18.8^0

Br	0.475181000000	10.277294000000	17.577698000000
Mn	-0.942112000000	9.425869000000	19.532590000000
Cl	3.422549000000	9.050341000000	22.131399000000

O	-2.624386000000	8.479840000000	21.776478000000
O	-0.715761000000	6.686154000000	18.398717000000
O	-3.343507000000	9.963889000000	17.888529000000
O	0.831301000000	9.244376000000	20.583341000000
N	-0.762451000000	11.329204000000	20.305915000000
N	2.114081000000	13.974914000000	23.145933000000
N	6.582436000000	15.884176000000	25.898720000000
C	-1.945134000000	8.857622000000	20.896936000000
C	-0.806984000000	7.761662000000	18.849337000000
C	-2.392960000000	9.745984000000	18.540543000000
C	-1.592437000000	12.373014000000	20.152643000000
H	-2.483022000000	12.208601000000	19.548954000000
C	-1.334110000000	13.627330000000	20.735021000000
H	-2.041527000000	14.440465000000	20.573356000000
C	-0.193603000000	13.812890000000	21.505084000000
H	0.032401000000	14.771299000000	21.971162000000
C	0.695516000000	12.731908000000	21.686070000000
C	1.930948000000	12.829569000000	22.471882000000
C	2.754037000000	11.655027000000	22.552450000000
H	3.633645000000	11.668905000000	23.192726000000
C	2.412633000000	10.468112000000	21.933653000000
C	1.210230000000	10.331314000000	21.151376000000
C	0.373294000000	11.511125000000	21.051470000000
C	3.262565000000	14.387333000000	23.742541000000
C	4.606827000000	14.013897000000	23.399314000000
H	4.784888000000	13.377936000000	22.532453000000
C	5.690298000000	14.526591000000	24.080480000000
H	6.693091000000	14.263734000000	23.748759000000
C	5.517534000000	15.423383000000	25.190042000000
C	4.181757000000	15.845394000000	25.499907000000
H	4.005756000000	16.555760000000	26.304874000000
C	3.111276000000	15.370502000000	24.777183000000
H	2.099367000000	15.703218000000	25.014000000000
C	6.394270000000	16.843861000000	26.997508000000
H	5.947566000000	17.779191000000	26.629622000000
H	7.368838000000	17.068639000000	27.437042000000
H	5.745261000000	16.418753000000	27.776753000000
C	7.951861000000	15.462711000000	25.566135000000
H	8.040081000000	14.368088000000	25.599889000000
H	8.637728000000	15.893302000000	26.299679000000
H	8.238010000000	15.816768000000	24.564289000000

C1-C2-N-C3 = 158.6^0

Br	1.505521000000	9.973245000000	17.461870000000

Mn	-0.186984000000	9.072425000000	19.165842000000
Cl	3.529539000000	9.277177000000	22.605925000000
O	-2.218943000000	8.079675000000	21.074014000000
O	0.510131000000	6.312932000000	18.305514000000
O	-2.221908000000	9.247439000000	17.021643000000
O	1.323757000000	9.144936000000	20.546789000000
N	-0.351317000000	11.028831000000	19.814243000000
N	1.998555000000	14.058953000000	22.996072000000
N	1.098418000000	19.459984000000	21.914873000000
C	-1.398127000000	8.476731000000	20.334642000000
C	0.238718000000	7.397156000000	18.650392000000
C	-1.419032000000	9.174489000000	17.873743000000
C	-1.265669000000	11.942215000000	19.452917000000
H	-2.007285000000	11.633950000000	18.718383000000
C	-1.290086000000	13.229796000000	20.013023000000
H	-2.080732000000	13.921113000000	19.722288000000
C	-0.320027000000	13.604838000000	20.933018000000
H	-0.360285000000	14.592986000000	21.384864000000
C	0.706538000000	12.697279000000	21.281094000000
C	1.746188000000	12.939268000000	22.297511000000
C	2.536693000000	11.810569000000	22.708080000000
H	3.258654000000	11.985314000000	23.505720000000
C	2.464893000000	10.573742000000	22.106139000000
C	1.493538000000	10.297958000000	21.086122000000
C	0.615023000000	11.394517000000	20.716066000000
C	1.753143000000	15.345274000000	22.641204000000
C	1.700325000000	15.868077000000	21.305337000000
H	1.864792000000	15.196221000000	20.462856000000
C	1.526748000000	17.213643000000	21.067584000000
H	1.550592000000	17.574367000000	20.041161000000
C	1.335112000000	18.142112000000	22.149158000000
C	1.433374000000	17.633166000000	23.486737000000
H	1.335340000000	18.305400000000	24.336659000000
C	1.678170000000	16.298059000000	23.712438000000
H	1.774844000000	15.924024000000	24.732778000000
C	0.923190000000	20.401087000000	23.032500000000
H	0.091472000000	20.083513000000	23.677284000000
H	0.694273000000	21.389049000000	22.626195000000
H	1.840058000000	20.469056000000	23.636298000000
C	1.049441000000	19.986931000000	20.542644000000
H	2.018144000000	19.852915000000	20.038597000000
H	0.820884000000	21.054647000000	20.586709000000
H	0.267152000000	19.481566000000	19.959120000000

C1-C2-N-C3 = 206.2^0

Br	1.228369000000	10.275715000000	17.816458000000
Mn	-0.668673000000	9.734836000000	19.451867000000
Cl	3.247827000000	8.935083000000	22.569422000000
O	-2.906378000000	9.137552000000	21.294708000000
O	-0.603605000000	6.936363000000	18.449172000000
O	-2.554920000000	10.509433000000	17.305839000000
O	0.804593000000	9.365107000000	20.838882000000
N	-0.356190000000	11.637796000000	20.195533000000
N	2.571601000000	13.831840000000	23.564300000000
N	-0.162295000000	18.196751000000	25.721462000000
C	-2.007594000000	9.378855000000	20.579039000000
C	-0.634229000000	8.035863000000	18.846762000000
C	-1.812026000000	10.200290000000	18.159399000000
C	-0.926701000000	12.783759000000	19.794558000000
H	-1.701800000000	12.708291000000	19.034356000000
C	-0.522980000000	14.032843000000	20.297497000000
H	-0.977447000000	14.939135000000	19.897985000000
C	0.447684000000	14.100361000000	21.287482000000
H	0.769508000000	15.067107000000	21.669485000000
C	1.021560000000	12.907430000000	21.784278000000
C	2.109450000000	12.845518000000	22.775127000000
C	2.822880000000	11.605815000000	22.888973000000
H	3.692283000000	11.595663000000	23.546524000000
C	2.392475000000	10.437340000000	22.295442000000
C	1.249768000000	10.417449000000	21.424375000000
C	0.622753000000	11.699780000000	21.154312000000
C	1.839727000000	14.878717000000	24.028642000000
C	0.414092000000	14.888358000000	24.198152000000
H	-0.158762000000	14.001119000000	23.931676000000
C	-0.236483000000	15.959201000000	24.764972000000
H	-1.310402000000	15.896169000000	24.928273000000
C	0.485720000000	17.129163000000	25.185796000000
C	1.914708000000	17.111480000000	25.056014000000
H	2.502833000000	17.965653000000	25.385413000000
C	2.559251000000	16.014447000000	24.529021000000
H	3.647397000000	16.007316000000	24.446638000000
C	0.587331000000	19.343990000000	26.256416000000
H	1.281230000000	19.020212000000	27.045414000000
H	-0.122382000000	20.056373000000	26.683834000000
H	1.156635000000	19.845063000000	25.459816000000
C	-1.629765000000	18.215175000000	25.820707000000
H	-2.084892000000	18.022483000000	24.839931000000
H	-1.944313000000	19.203241000000	26.165652000000

H	-1.985362000000	17.459290000000	26.537858000000

C1-C2-N-C3 = 336.0^0

Br	1.804042000000	10.659401000000	17.401360000000
Mn	-0.177299000000	9.788984000000	18.775411000000
Cl	3.407172000000	9.051629000000	22.308496000000
O	-2.507912000000	8.827875000000	20.325898000000
O	0.244937000000	7.119006000000	17.535531000000
O	-1.931396000000	10.591409000000	16.530000000000
O	1.179944000000	9.418909000000	20.287228000000
N	-0.136606000000	11.630796000000	19.703945000000
N	1.947913000000	13.911465000000	23.424498000000
N	3.710053000000	14.443447000000	28.697662000000
C	-1.573281000000	9.208964000000	19.726358000000
C	0.077376000000	8.166829000000	18.027433000000
C	-1.239759000000	10.270706000000	17.421395000000
C	-0.792798000000	12.751297000000	19.363536000000
H	-1.466740000000	12.686259000000	18.511455000000
C	-0.623525000000	13.961253000000	20.061857000000
H	-1.174138000000	14.842480000000	19.733398000000
C	0.229689000000	14.017105000000	21.155772000000
H	0.366680000000	14.933947000000	21.728395000000
C	0.942679000000	12.857203000000	21.528550000000
C	1.840645000000	12.795485000000	22.685310000000
C	2.581589000000	11.582026000000	22.880814000000
H	3.362725000000	11.561779000000	23.639419000000
C	2.407040000000	10.471218000000	22.078757000000
C	1.430849000000	10.443162000000	21.020049000000
C	0.731980000000	11.687400000000	20.762345000000
C	2.395483000000	13.948461000000	24.706295000000
C	2.404053000000	12.852117000000	25.636158000000
H	1.988391000000	11.891124000000	25.335696000000
C	2.821261000000	13.015259000000	26.937950000000
H	2.747333000000	12.173043000000	27.623100000000
C	3.285715000000	14.287507000000	27.416239000000
C	3.237466000000	15.398128000000	26.507736000000
H	3.553512000000	16.386133000000	26.836950000000
C	2.786264000000	15.231559000000	25.218375000000
H	2.748694000000	16.083554000000	24.537598000000
C	4.033786000000	15.776946000000	29.227739000000
H	4.899320000000	16.207111000000	28.702807000000
H	4.277693000000	15.680994000000	30.288517000000
H	3.175370000000	16.455721000000	29.122145000000
C	3.792606000000	13.293520000000	29.610758000000

H	2.788371000000	12.930812000000	29.879758000000
H	4.310139000000	13.606454000000	30.520931000000
H	4.359532000000	12.475539000000	29.147650000000

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